

Refinement of the Structure of a Grossularite Garnet

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(Received 5 November 1957)

Grossularite, a garnet with ideal formula $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$, crystallizes in the cubic system, space group $Ia\bar{3}d-O_h^{10}$ with $a = 11.874 \pm 0.004$ Å and eight formula weights per unit cell. The Ca, Al and Si atoms are in special positions; the undetermined positional and thermal parameters (except B_{Al}) have been refined by the method of least squares. Only the 101 general structure factors particularly sensitive to the positional coordinates of the oxygen atom were used in this process. The final coordinates $x = -0.0389$, $y = 0.0456$, $z = 0.1524$, correspond to $R = 0.126$; the Si-O distance is 1.64 Å, the nominally-Al-O distance is 1.95 Å and the Ca-O distances are 2.33 and 2.49 Å. The limits of error in cation-O distances are ± 0.02 Å, in O-O distances are ± 0.03 Å and in cation-O-orientation angles are $\pm 1^\circ$.

None of the oxygen polyhedra is regular, although the space group would allow the tetrahedra and octahedra to be regular simultaneously. Unlike the case of yttrium-iron garnet, the octahedra are more nearly regular than the tetrahedra; both of these polyhedra are more regular and the CaO_8 dodecahedra less regular than the corresponding oxygen polyhedra in yttrium-iron garnet. These observations lead to a prediction regarding structural relationships in the garnets uvarovite, $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$, and andradite, $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$.

In the least-squares refinement of this structure, it is observed that two very different data-weighting methods lead to equivalent results.

Introduction

The recent discovery of ferrimagnetism in the rare-earth-iron garnets (Bertaut & Forrat, 1956; Geller & Gilleo, 1957a) has renewed interest in all compounds with the garnet-type structure. A quantitative understanding of the magnetic nature of a rare-earth-iron garnet requires a knowledge of the accurate positions of the atoms. However, atomic positions cannot in themselves establish bond types in this structure. It is improbable that even an apparently accurate evaluation of the three-dimensional electron-density distribution would give this information. However, with the structural knowledge as a basis, other types of physical measurement could lead to an understanding of the bonding in these compounds. The refinement of the structure of yttrium-iron garnet (Geller & Gilleo, 1957b) from three-dimensional data established certain relationships between the structure and its magnetic properties. It showed also that the ligand fields at the magnetic ions did not establish the regular polyhedra allowed by the space group to which the structure belongs. The oxygen octahedra and tetrahedra are very irregular, although the Fe-O distances within each are equal. The relationship of the oxygen polyhedra in a silicate garnet to that in a rare-earth-iron garnet is of particular interest, since as recently as 1951 the existence of even yttrium-aluminum garnet was in doubt (see Yoder & Keith, 1951). In the silicate garnets, the SiO_4 tetrahedra are not linked directly to each other as in most silicates; each oxygen is at the corner of only one tetrahedron.

The garnet structure is completely determined by

three oxygen-atom positional parameters and the thermal vibration parameters of the oxygen and the three other atoms. With the use of powder X-ray photography, Menzer (1928) determined the positional parameters in a number of natural silicate garnets, including a grossularite. However, the accuracy of Menzer's parameters is only about $\pm(0.1-0.2)$ Å. The object of the present study is an accurate determination of the positional parameters from single crystal data.

Crystal data

Grossularite, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$ (ideal formula) has F.W. = 450.47; $D_m = 3.576$ g.cm.⁻³ (Skinner (1956) reports 3.594 g.cm.⁻³ for pure synthetic grossularite), $D_X = 3.574$ g.cm.⁻³ for the ideal formula*. The crystal is cubic with $a = 11.874 \pm 0.004$ Å, and contains eight formula weights per unit cell; (hkl) is present only with $h+k+l = 2n$, (hhl) only with $2h+l = 4n$, and $(0kl)$ only with $k, l = 2n$. The space group is hence taken as $Ia\bar{3}d-O_h^{10}$. The absorption coefficient for Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) is 244.4 cm.⁻¹. Volume of the unit cell is 1674.1 Å³; total number of electrons per cell, $F(000)$, is 1792.

A chemical analysis† by E. Bloom, Jr. of these Laboratories, of the Chihuahua, Mexico, grossularite specimen‡ used in the present investigation yielded:

* D_X based on the chemical analysis given below is 3.697 g.cm.⁻³.

† A spectroscopic analysis made by W. Hartman indicated, in addition to the above, an impurity of 0.01-0.3% Mn.

‡ Obtained from Ward's Natural Science Establishment.

	Weight % found	Weight % predicted (ideal formula)
SiO ₂	38.83	40.02
CaO	34.81	37.35
Al ₂ O ₃	18.84	22.63
Fe ₂ O ₃	4.36	0
TiO ₂	0.33	0
MgO	2.55	0
Total	99.72	100.00

This grossularite is optically inhomogeneous; some small crystals show birefringence, others are entirely isotropic. The spherical crystal used in the X-ray analysis is light yellow, transparent and isotropic.

Refinement of the structure

The aluminum, calcium and silicon atoms lie respectively in the 16(*a*), 24(*c*), and 24(*d*) positions of *Ia3d*. In the absence of disorder, the positions of these atoms may hence be taken as 0, 0, 0; $\frac{1}{8}$, 0, $\frac{1}{4}$; and $\frac{3}{8}$, 0, $\frac{1}{4}$. The oxygen atom, in 96(*h*), has the unknown coordinates *x*, *y*, *z*. Menzer (1928) found these coordinates to have the values: -0.04 ± 0.01 , 0.055 ± 0.01 , 0.14 ± 0.015 for grossularite, andradite, almandite and spessartite.

An accurate determination of the position of the oxygen atom in the presence of the heavier atoms is possible by considering only those structure factors for which *h*, *k* are odd, and *l* is even (*h*, *k*, *l* permutable). Atoms in 16(*a*) contribute nothing to such reflections. Atoms in 24(*d*) have identical structure amplitudes with those in 24(*c*) but *opposite* signs for reflections with $l = 4n + 2$. The net contribution of the Al, Ca and Si atoms to such structure factors is then of the form $\pm 8(f_{\text{Ca}}^T - f_{\text{Si}}^T) \sin \frac{1}{4}\pi h$, where f_{Ca}^T , f_{Si}^T are the atomic scattering factors of Ca and Si at room temperature. These three atoms make no contribution to reflections with *h*, *k* odd and $l = 4n$ (*h*, *k*, *l* permutable). The two classes of reflections described are hence particularly sensitive to the oxygen positional coordinates.

It was apparent at the outset that the values of *x*, *y*, *z* for the oxygen atom in grossularite would be different from those in isostructural yttrium-iron garnet (Geller & Gilleo, 1957*b*). Nevertheless, the latter values (Table 1) were a reasonable starting point. The remaining parameters required to define completely the crystal structure of grossularite are the temperature factors of the four kinds of atoms present. The atomic scattering factors used, namely those of Berghuis *et al.* (1955) for Si⁴⁺, those of James & Brindley (1931) for Ca²⁺ and an arbitrarily modified Berghuis *et al.* (1955) curve for O²⁻, in which $f_{\text{O}^{2-}} = 10.00$ at $\sin \theta/\lambda = 0$ and $f_{\text{O}^{2-}} = f_{\text{O}}$ at $\sin \theta/\lambda = 0.20$, were therefore multiplied by the expression $\exp[-B_j(\sin \theta/\lambda)^2]$. The values chosen for *B_j* are 1.0 Å² for silicon, 0.5 Å² for calcium and 2.0 Å² for oxygen, by comparison with the corresponding values

of 0.63, 0.16 and 2.05 Å² for iron, yttrium and oxygen in yttrium-iron garnet. The choice of reflections used in this analysis precludes measuring the aluminum atom temperature factor.

The method of least squares is admirably suited to the present problem of refinement with a limited set of general structure factors. In applying this method, two entirely different weighting systems were used. The first follows that of Geller & Gilleo (1957*b*) in which all observed structure factors $F(hkl)$ are given weight 1.00, those of form $F(hhl)$ weight 0.50 (in accordance with the multiplicity of these planes), unobserved $|F(hkl)| \leq 4.0$, weight 0.20 and for $4.0 < |F(hkl)| \leq 8.0$, weight 0.01. The second system follows that of Abrahams (1955) in which, for $|F(hkl)| \geq 24$, $w(hkl) = 10^4/|F(hkl)|^2$; for $|F(hkl)| < 24$, $w(hkl) = 31$ and for unobserved $F(hkl)$, $w(hkl) = 0.3$ (1% maximum weight).

The refinement process, using each set of weights separately, converged rapidly, using the Sayre least-squares program for the IBM 704 machine. The auxiliary program for space group *Ia3d* was worked out by Miss D. C. Leagus of these Laboratories. After six iterations $R (= \sum |F_o| - |F_c| \div \sum |F_o|)$ became rather constant, and, more important, the largest shifts in the parameters became less than their standard deviations. The value of *R* fell from 0.477 with the initial parameters, to 0.122 for the parameters derived using the first (G. G.) weights, and to 0.132 for those with the second (A.) set of weights (see Table 1).

Table 1. Positional and thermal parameters for grossularite

Parameters	<i>x</i> _O	<i>y</i> _O	<i>z</i> _O	<i>B</i> _O (Å ²)	<i>B</i> _{Si} (Å ²)	<i>B</i> _{Ca} (Å ²)
Initial	-0.0274	0.0572	0.1492	2.00	1.00	0.50
Sixth set (G.G.)	-0.0386	0.0456	0.1522	1.79	0.62	0.76
Sixth set (A.)	-0.0391	0.0456	0.1525	1.98	0.55	0.79
Final set*	-0.0389	0.0456	0.1524	1.88	0.59	0.77

* Average (G.G.) and (A.).

The value of *R* corresponding to the final set of coordinates (Table 1) is 0.126 for all 101 recorded reflections; for the 37 observed reflections resulting from oxygen-ion contributions only, *R* is 0.119.

Accuracy of the determination

The standard deviations in the coordinates (Table 2) were derived by the least-squares method in the usual way; for example, see Abrahams (1955).

Table 2. Standard deviations in the atomic coordinates

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$ (Å ²)
G.G. weights				
O	0.00054	0.00053	0.00052	0.096
Si	0	0	0	0.066
Ca	0	0	0	0.051
A. weights				
O	0.00043	0.00042	0.00041	0.093
Si	0	0	0	0.048
Ca	0	0	0	0.038

The standard deviation in any oxygen-cation distance results only from that in the oxygen-atom position (disregarding errors in the lattice constant and in composition) and hence is ± 0.006 Å. In oxygen-oxygen contacts, the standard deviation is ± 0.009 Å, and in cation-oxygen-cation angles it is about $20'$, the limits of error in cation-oxygen distances hence being ± 0.02 Å, in oxygen-oxygen distances ± 0.03 Å, and in angle $\pm 1^\circ$.

Interionic dimensions

The distances and angles given in Table 3 are obtained from the final set of coordinates (Table 1).

Experimental

The lattice constants were measured by the Straumanis method, using a Norelco 114.59 mm. powder camera. All intensity records were made by the equi-inclination Weissenberg technique, using Cu $K\alpha$ radiation with a three-film pack (Eastman Kodak Industrial Type K film). The normal film:film ratio was taken as 3.5:1 with this radiation, due correction being made for obliquity. The single spherical crystal of radius 0.023 cm. used throughout was prepared in a Bond (1951) sphere grinder. Intensity measurements were made visually and corrected by the Lorentz-

Table 3. *Interionic distances and angles in grossularite*

SiO ₄ tetrahedron	Si-O	1.64(4) Å*
	O-O	2.56(2), 2.73(4)
AlO ₆ octahedron	Al-O	1.95(6)
	O-O	2.71(6), 2.79(6)
CaO ₈ dodecahedron	Ca-O	2.33(4), 2.49(4)
	O-O	2.56(2), 2.79(4), 2.85(2), 2.97(4), 3.99(1), 4.14(1), 4.24(4)
	Ca-Al	3.32(4)
	Ca-Si	2.97(2), 3.64(4)
	Al-Si	3.32(6)
	Si-O-Al	135.7°
	Ca-O-Ca	97.9
	Ca-O-Si	95.4, 122.1
	Ca-O-Al	96.1, 101.6

* The numbers in parentheses indicate the frequency of occurrence.

polarization, the Tunell (1939) rotation and the Bond (1958) absorption factors before conversion to relative structure factors. The ratio of maximum to minimum intensity in hkl is 380:1; in $hk3$, 200:1; in $hk5$, 400:1; and in $hk7$, 96:1. Common sets of reflections were used to place the 10I structure factors on a single relative scale; in this process the average agreement factor between common sets was 0.088. The scale factor required to put the relative scale on an absolute basis was obtained as an additional parameter in the

Table 4. *Observed and calculated structure amplitudes of grossularite*

(hkl)	F_o	F_c	(hkl)	F_o	F_c	(hkl)	F_o	F_c	(hkl)	F_o	F_c
211	<5.1	-8.6	961	25.4	24.0	653	43.9	44.3	655	22.1	22.2
611	154.3	167.3	11,6,1	<6.1	-0.9	853	71.7	-72.0	10,5,5	16.4	-10.9
10,1,1	21.6	25.0	13,6,1	6.6	-4.4	10,5,3	31.2	25.7			
14,1,1	8.2	-6.0				12,5,3	21.8	17.8	765	42.7	-38.2
			871	7.5	-5.4	14,5,3	19.0	-18.2	965	13.6	13.7
321	*	15.1	10,7,1	28.3	-25.2	763	9.3	-9.2	11,6,5	12.4	-14.1
521	107.8	-111.9	12,7,1	9.4	8.4	963	38.0	31.5	13,6,5	22.8	25.7
721	5.0	3.8				11,6,3	57.5	-47.2	875	25.7	23.0
921	19.4	-20.5	981	28.7	24.0	13,6,3	<3.7	6.3	10,7,5	5.4	-3.3
11,2,1	7.1	8.9	11,8,1	22.9	-20.3				12,7,5	<3.4	-0.3
13,2,1	<7.3	-0.8				873	48.3	42.8	985	22.5	-17.2
15,2,1	19.4	24.9	10,9,1	4.9	-8.0	10,7,3	12.4	11.8	11,8,5	23.4	20.5
			12,9,1	11.8	-9.5	12,7,3	27.2	-18.8			
431	98.3	109.9	11,10,1	11.7	12.3				10,9,5	<4.0	-4.8
631	11.9	-11.4				983	14.9	-13.7			
831	<8.1	-3.5	323	105.8	-98.2	11,8,3	17.8	-17.1	727	64.6	45.4
10,3,1	17.7	-13.3	523	101.9	-112.8				927	<6.8	-1.6
12,3,1	23.1	19.8	723	8.7	-12.6	10,9,3	<4.6	2.2	11,2,7	23.8	23.7
14,3,1	24.5	22.3	923	37.9	-34.7				13,2,7	31.0	-28.6
			11,2,3	7.4	6.9	11,10,3	8.1	-0.5			
541	<7.5	8.7	13,2,3	22.8	-20.9				947	24.1	-19.4
741	55.9	60.2				525	62.9	-58.9	11,4,7	42.2	33.1
941	73.0	71.1	633	39.7	-40.8	725	28.4	-25.8			
11,4,1	36.0	-33.7	723	8.7	-12.6	925	7.5	3.5	767	28.8	21.8
13,4,1	4.7	1.3	923	37.9	-34.7	11,2,5	18.9	-13.7	967	55.7	42.8
			11,2,3	7.4	6.9	13,2,5	25.4	20.9	11,6,7	19.3	-17.9
651	29.3	31.6	13,2,3	22.8	-20.9				10,7,7	17.2	14.4
851	51.7	51.8				543	27.9	-37.3			
10,5,1	18.5	-16.4	633	39.7	-40.8	743	21.8	-26.1			
12,5,1	5.5	-7.3	723	8.7	-12.6	943	28.7	-29.4			
14,5,1	8.8	-2.6	923	37.9	-34.7	11,4,3	<7.0	1.1			
			11,2,3	7.4	6.9	13,4,3	4.7	-5.7			
761	46.9	43.5							987	<4.5	0.6

* Not observed; lies on heavy streak.

least-squares process. The complete set of observed structure factors is collected in Table 4 under F_o . The calculated structure factors based on the final set of coordinates, using the atomic form factors previously discussed, are given in Table 4 under F_c .

A number of forbidden reflections were found on the fifth-layer photograph. These were shown to be double reflections, for on re-examination of this layer with Co $K\alpha$ radiation they disappeared.

Discussion

The Si-O distance of 1.64 Å in grossularite agrees well with recent determinations of this length in other crystals* although it is not clear whether the Si-O bond is identical in silicates with and without isolated SiO_4 tetrahedra. It is unlikely that the presence of 0.33% TiO_2 would affect significantly the tetrahedral atom-oxygen distance. The octahedral-site distances could, however, be affected by the 4.36% Fe_2O_3 present† in the structure, in which the iron atoms presumably substitute for aluminum. The effect of the impurities on the Ca-O distances is uncertain, but the octahedral ion-oxygen ion distance should be liable to an increase of not more than 0.02 Å, as compared with a grossularite of ideal formula. The Al-O distance in a pure grossularite, which could therefore be taken as 1.93–1.95 Å, agrees well with other octahedral Al-O distances.‡

In yttrium-iron garnet, the oxygen octahedron has two sets of O-O distances differing by 0.31 Å; the AlO_6 octahedron in the grossularite is more nearly regular with the two sets of distances differing by only 0.08 Å. In yttrium-iron garnet, the FeO_4 tetrahedron has two sets of O-O distances differing by 0.29 Å; in grossularite, the SiO_4 tetrahedron is more regular with the difference being 0.17 Å. On the other hand, the dodecahedron of oxygen atoms about a calcium is apparently more irregular than that about an yttrium ion.§ It is particularly interesting to note that the two different Y-O distances in yttrium-iron garnet are

* For example, Newnham & Brindley, 1956; Seeman, 1956; MacGillavry *et al.*, 1956; Zussman, 1955; Bailey & Taylor, 1955; Steinfink, Post & Fankuchen, 1955; Hahn & Buerger, 1955.

† The amount of Fe_2O_3 present in a 0.5 g. sample of this mineral is not necessarily identical with the corresponding amount in the light yellow transparent single crystal used in this investigation.

‡ Geller, 1957; Delorme, 1956; MacGillavry *et al.*, 1956; Newnham & Brindley, 1956. A recent neutron-diffraction determination of the oxygen parameters in yttrium-aluminum garnet (Prince, 1957) leads to an octahedral Al-O distance of 1.95 Å and a tetrahedral Al-O distance of 1.77 Å. The percentage change in Al-O distance with change from CN(6) to CN(4) is greater than for the Fe-O distances in yttrium-iron garnet. In as yet unpublished work, E. Prince of these Laboratories has found octahedral Al-O distances of 1.92 and 1.94 Å in ZnAl_2O_4 and MnAl_2O_4 respectively.

§ The difference in size of the unit cells of the two garnets has been considered in this comparison of the regularity of oxygen polyhedra.

2.37 and 2.43 Å, a difference of 0.06 Å, whereas the Ca-O distances in grossularite differ by 0.16 Å. The Si-O-Al angle, 135.7°, is considerably larger than the Fe-O-Fe angle of 126.6° in yttrium-iron garnet. A view of the three kinds of oxygen polyhedra and the surroundings of an oxygen ion in grossularite is shown in Fig. 1.

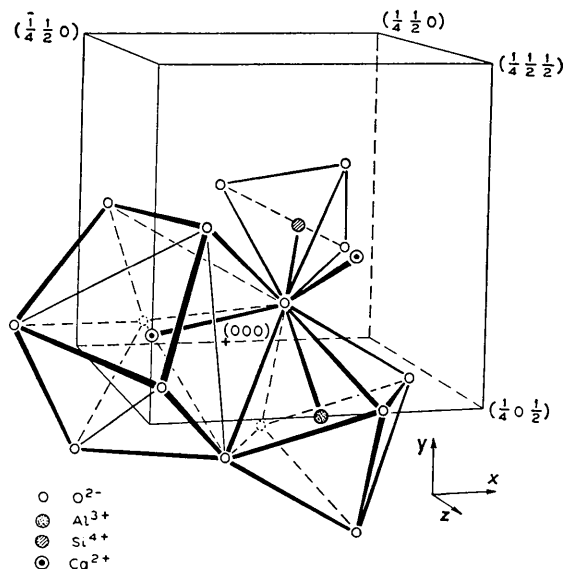


Fig. 1. The surroundings of an oxygen ion in grossularite. For the sake of clarity, one of the oxygen dodecahedra about a calcium ion is omitted.

It is very probable that the differences in the two structures may be attributed mainly* to the relative 'sizes' of the atoms, or ions, on the octahedral and tetrahedral sites. The average Ca-O distance, 2.41 Å, is close to the average Y-O distance, 2.40 Å. The difference between the ratios Ca-O/Al-O of 1.24 and Y-O/Fe-O of 1.20 is small as compared with that between Al-O/Si-O of 1.18, and the two Fe-O distances of 1.06. It might be predicted that uvarovite, $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$, with a large ratio Cr-O/Si-O, has more nearly regular octahedra and tetrahedra than has grossularite. In andradite, $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$, the octahedra and tetrahedra are either more regular than in uvarovite, or, alternatively the length of the set of two O-O distances in the tetrahedron is greater than that of the set of four distances (Table 3).

With regard to the two methods of weighting of the data for least-squares calculation, it is seen that two very dissimilar methods have led to results equivalent within experimental error. The largest discrepancy is in the B values of the oxygen atom. The difference in R values for grossularite (12.6%) and yttrium-iron garnet (9.2%) is not felt to be significant.

* Electrostatic effects must also be involved since there is a difference in the valencies of the ions in the 24(c) and 24(d) sites in the two structures.

It is a pleasure to thank E. Prince for allowing us to use his unpublished results on MnAl_2O_4 and ZnAl_2O_4 , H. E. Earl for preparing the spherical crystal, C. E. Miller for taking and measuring the powder photograph, H. J. Seubert for drawing Fig. 1, and A. H. Hatch of the Service Bureau Corporation for carrying out the IBM calculations.

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Thermal Expansion of Hexamethylbenzene

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(Received 31 July 1957 and in revised form 23 December 1957)

From X-ray measurements of the thermal expansion of hexamethylbenzene, the principal coefficients of thermal expansion have been determined in magnitude and direction, the values being 2·09, 0·48 and $0\cdot30 \times 10^{-4}$ deg.⁻¹. The increase in distance between molecules linked by van der Waals forces varies from 3·3 to $6\cdot5 \times 10^{-4}$ Å deg.⁻¹.

Although detailed structural investigations such as those of Cruickshank (1956) on anthracene are necessary for a complete description of the thermal movement of the atoms or molecules forming a crystal, some conclusions may, in simple cases, be drawn from the thermal expansion of the crystal lattice.

Hexamethylbenzene affords such a case (Brockway & Robertson, 1939). The molecules constituting this crystal are highly symmetrical ($6/m$) and lie very nearly in close-packed layers in the (001) plane. The stacking of these layers is, however, such that the crystal is triclinic, ($P\bar{1}$), with one molecule per unit cell. Thus the orientation of the expansion ellipsoid is not determined by the symmetry requirements of the crystal.

A sample of hexamethyl benzene kindly supplied by Messrs I. C. I., was purified by Prof. A. R. Übbelohde, to whom the author is indebted for the material

used and also for the following note regarding its preparation:

'The difficulties in the purification of hexamethylbenzene for measurement of the thermal properties arise from its comparatively low lattice energy. This permits the crystals to pack related molecules as impurities in solid solution, and to retain solvent molecules in solid solution unless these have a very different molecular shape. The sample available was therefore purified by two successive chromatographic treatments on a column of activated alumina (Type H, Peter Spence). In the first fractionation the elutrient was 50% benzene and 50% petroleum ether (b.p. 80–100° C.); ten equal fractions were collected. After evaporation of solvent and determination of the melting points, the two best fractions that gave large crystals free from efflorescence and creep (m.p. 163·4–163·6° C.), and that were free from colour, were